The electronic structure of $YBa_2Cu_4O_8$ studied by soft X-ray absorption and emission spectroscopies

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INTRODUCTION

Soft X-ray emission provides a means of elemental selectivity, chemical sensitivity to separate the partial contributions to the total density of states. This technique probes the bulk property of the matter owing to the large penetration depth of photons. Recently, synchrotron radiation sources producing intense tunable monochromatized X-ray beams have opened up new possibilities for soft X-ray emission spectroscopy (XES) [1]. The ability to tune the excitation with narrow bandpass allows one to discriminate the close lying core excited states, and thereby to separate e.g. chemical shifted species in the emission spectrum.

In the previous investigations, resonant SXES was used to study the electronic structure of $La_{2-x}Sr_xCuO_4$ [2], $Bi_2Sr_2CaCu_2O_{8+\delta}$, and $Tl_2Ba_2CaCu_2O_8$ [3]. It has been demonstrated that the spectral shape of the O $K\alpha$ emission depends on the relative number of excited specific-site oxygen atoms. Tuning the excitation photon energy to the specific edges enhances the excitation of one particular chemically shifted species, such as separating in-plane oxygen from out-of-plane oxygen in $La_{2-x}Sr_xCuO_4$ cuprates. Thus, the features in the XAS spectrum related to the O unoccupied states can be characterized in terms of the density of states projected on individual oxygen sites [2-3].

In the present paper, we study the electronic structure of superconductors $YBa_2Cu_4O_8$ with a combination of XAS and XES. In the following, we will adopt the notation of O(1), O(2), O(3), and O(4) for, respectively, the oxygen sites between the Cu(1) atoms in the chain, those of the plane, and the apical sites.

EXPERIMENT

The $YBa_2Cu_4O_8$ [4] were prepared by solid-state sintering of the starting materials at 940˚C for one week, annealing at 400˚C in O_2 for two days to obtain a fully oxidized sample. The samples were characterized by X-ray diffraction and no impurities could be detected. The oxygen content was determined by iodometry.

The measurements were performed at beamline 7.0 at ALS, LBNL. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator [5]. The XAS spectra were obtained by recording the fluorescence-yield with 0.3 eV resolution and normalized to the photocurrent of a clean gold mesh to correct the intensity loss of the excitation beam. The O $K\alpha$ emission was recorded using a high-resolution grazing-incidence grating fluorescence spectrometer [6]. The incidence

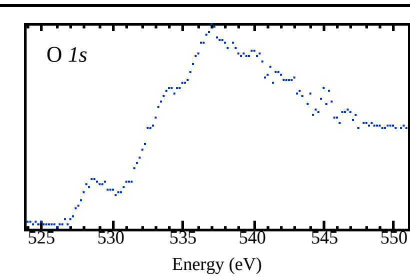

Figure 1. The O *1s* XAS spectrum of $YBa_2Cu_4O_8$.

angle of the photon beam was about 20˚ to the sample surface in order to reduce self-absorption effect. The X-ray fluorescence was detected at the direction perpenticular to the incident photon beam in the horizontal plane. The resolution was set to 0.5 eV and 1.2 eV at the energy of 530 eV, respectively, for the monochromator and spectrometer. Zn $L\alpha$ and $L\beta$ emission lines were recorded in second order for energy calibration of O $K\alpha$ spectra.

RESULTS AND DISCUSSION

The O *1s* XAS spectrum of $YBa_2Cu_4O_8$ are displayed in Figure 1. O *1s* spectrum reflects the unoccupied O *2p* states. We observe that an absorption pre-peak appears already at 528.5 eV which is an indication of induced O *2p* holes upon oxygen doping. This is similar to that in the O *1s* absorption edges of $La_{2-x}Sr_xCuO_4$ [7-9], which was interpreted by a doping-induced shift of the Fermi level into the valence band, the creation of the holes in the valence band, and a transfer of spectral weight from states in the upper Hubard band to the upper edge of the valence band [10-12]. The first absorption peak in the XAS spectrum of $YBa_2Cu_4O_8$ is considerably broader than expected from experimental resolution (0.5 eV) and the lifetime width of the O *1s* state. It is most likely due to vibrational excitations and chemical shifts between different oxygen sites.

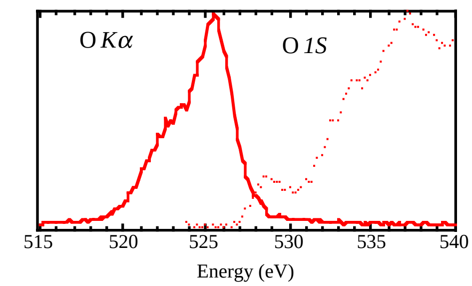

Figure 2. O $K\alpha$ XES and O *1s* XAS spectra of $YBa_2Cu_4O_8$ which map occupied and unoccupied states close to the Fermi level, respectively.

Figure 2 shows the valence-core XES spectrum along with XAS spectrum. In the case of $YBa_2Cu_4O_8$, the absorption-emission spectra show the unbroken density of states crossing the Fermi level, reflecting the metallic character of $YBa_2Cu_4O_8$.

O $K\alpha$ profiles, similar to those of $YBa_2Cu_3O_{6.94}$ [13], are also observed for $YBa_2Cu_4O_8$. This compound contains double Cu(1)-O(1) chains, thus having the larger number of O(1) atoms per unit cell. Same as for $YBa_2Cu_3O_{6.94}$, O $K\alpha$ spectra of $YBa_2Cu_4O_{8-\delta}$ do not show strong dependence on varying excitation energies (see in Figure 3). The spectra resemble that obtained with an electron beam in prior study [14]. Nevertheless, one can notice that the low-energy shoulder in 528.7-eV photon excited spectrum is less intense as compared to other spectra and extends somewhat more towards lower energies. Such a behavior is in agreement with band structure calculations for O(1) and O(4) (see for example, Ref [15]) and indicates a predominant contribution of these O atoms to the 528.7-eV peak of the O 1s absorption edge. Same as for $YBa_2Cu_3O_{6.94}$, this finding suggests a location of

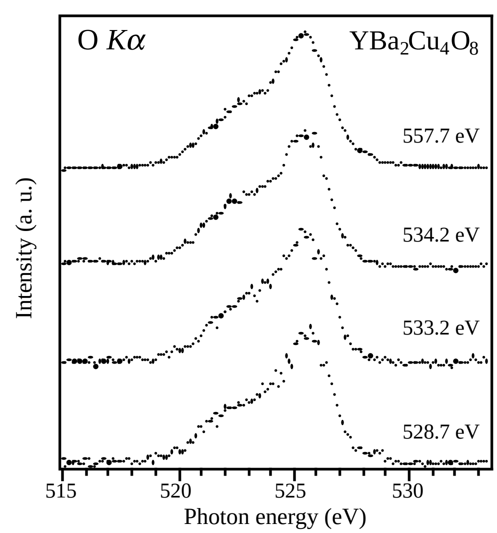

Figure 3. O $K\alpha$ XES spectra of $YBa_2Cu_4O_8$ recorded at different excitation energies near O *1s* threshold. The TEY spectrum at the O *1s* edge is shown at the top panel.

an appreciable amount of doping-induced holes at O(1) and O(4) sites and an importance of O(1)-Cu(1)-O(4) ribbons for superconducting properties of $YBa_2Cu_4O_8$.

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